On the Rate of Alcoholysis of Hydrosilanes

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where ρ is the fluidized bed density at the height of h cm. from the bottom, ρ_b and ρ_t are those at the bed-bottom and bed-top respectively, A is the cross sectional area of the bed, a is a constant, and ρ_b/ρ_t is approximately equal to the ratio of the weight of the maximum particle size by that of minimum one, contained in the bed. Thus it can be concluded that the density-distribution of fluidized bed is ascribed to the non-uniformity of the particles involved in the system. Accordingly uniform particles should be used to obtain the uniform density-distribution.

In the system of the two kinds of fluidized particles, they are separated in two layers, in the same manner as the system of two liquids which have poor solubility mutually. In this system the layer is richer in one component and *vice versa*.

This phenomenon is a peculiarity of fluidized bed which is distinguished from fixed bed or transporting powder.

In the system of same kinds or particles (and of different size) *i.e.*, coarse and fine sand system, they are separated into two layers more clearly in faster linear velocity of the fluidized fluid (gas or liquid) just as in water-trimethylamine system. In the case of the different species *i.e.* sand-carbon powder system, this tendency is inverse just as in water-phenol system. This character is the third phenomenon that the fluidized particles resemble to the liquid and also in this case it can be said that the temperature (as an intensive property) of fluidized particles correspond to the linear velocity of the fluidizing fluid (gas or liquid).

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12. On the Rate of Alcoholysis of Hydrosilanes

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The reaction rates of alcoholysis of six hydrosilanes, shown in Table 1, were investigated in the presence of the catalysts of HCl, KOH *etc.* in alcoholic solution at the temperature of 40-50°C, measuring the hydrogen evolved in course of the reaction.

In the case of HCl catalyst, this reaction was the first order with respect to silane and the 1.8th order as to HCl respectively, and the observed values of the first order rate constant and activation energy at the concentration of HCl 2.1 M are given in Table 1.

Table 1. Hydrosilane 0.373 *M*
HCl 2.10 *M*

Silane	$K_{50°}$ (1/min.)	E_A (kcal./mole)
$(C_2H_5)_3SiH$	0.0133	15.9
$(C_3H_7)_3SiH$	0.00903	16.5
$(C_4H_9)_3SiH$	0.00901	16.6
$(C_2H_5)_2(C_2H_5O)SiH$	0.0212	13.7
$(C_2H_5)(C_2H_5O)_2SiH$	0.0200	17.1
$(C_2H_5O)_3SiH$	0.00515	11.9

The experimental results obtained for the same silanes with KOH catalyst, are similarly shown in Table 2, but in this case, the order of the rate was the first with respect to both silane and KOH.

Table 2. Hydrosilane 0.2—0.4 *M*
KOH 0.0155 *M*

Silane	$K_{50°}$ (1/min.)	E_A(kcal./mole)
$(C_2O_5)_3SiH$	0.00181	14.3
$(C_3H_7)_3SiH$	0.000768	17.6
$(C_2H_5)_2(C_2H_5O)SiH$	0.175	9.72
$(C_2H_5)(C_2H_5O)_2SiH$	1.80	9.71
$(C_2H_5O)_3SiH$	8.64	10.4

These experimental results are satisfactorily explained as follows.

The rate determining step of this alcoholysis is in the cleavage of Si-H bond of silane, and prior to this cleavage, the basic reagent attacks the Si atom of this bond which has been polarized into $Si^{+\delta}-H^{-\delta}$.

Namely in the case of KOH catalyst, OH^- ion attacks the Si atom to give a complex and then Si-H bond of this complex is ruptured.

Accordingly, by the substitution in tri-alkyl silane with larger alkyl radicals, for example propyl or butyl radical having comparatively electron-repelling properties, the decrease of reaction rate and the increase of activation energy are caused, because by this substitution, the electoropositivity of Si atom is reduced, consequently the formation of complex is supressed.

Contrarily, the higher electropositivity of Si atom results from the replacement of alkyl radical with ethoxy radical being more electrophilic. Therefore, mono-ethoxy di-ethyl silane reacts more rapidly than tri-ethyl silane and its activation energy is small, however in both cases of di-ethoxy and tri-ethoxy silane activation energies are almost of the same magnitude as that of mono-ethoxy silane, in spite of regular increase of reaction rates.

This is probably ascribed to that the electropositivity of Si atom in complex is

excessively increased and subsequently the Si-H bond is electrostatically strengthened.

In the case of HCl catalyst, the reaction proceeds by the similar mechanism, but the basicity of reagent which attacks Si atom is weaker than that of OH^-, so, for the cleavage of Si-H bond the additional attack of alcoxonium ion on H atom in this bond is required. Consequently, the order of this reaction approaches to the second order with respect to the concentration of catalyst and the reactivity of silane is also affected by the strength of its Si-H bond. Thus, the effect of substituent on the rate is more complicated since the rate is affected by two factors mutually counteracting.

Now, it is deduced from above arguments that even in the case of acid catalyst, by using of more basic anion in place of Cl^-, the rate of cleavage is promoted and the order of its rate falls to the first order as to the catalyst as in the case of KOH.

In fact, this deduction coincides with the results observed qualitatively for the HBr catalyst in dioxane, that is, in this case the rate was markedly faster than in HCl, and of the 0.98 th order as to HBr.

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13. Iodine Catalyzed Aromatic Bromination. (II)

Bromination of Toluene

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In the preceding papers (This Bulletin, **28**, 71 (1952) ; *J.Am.Chem.Soc.*, **74**, 5995 (1952)), it was shown that the iodine catalyzed aromatic bromination proceeds according to the following rate laws

$$v=k[ArH][Br_2][BrI]^m \qquad (1)$$

$$v=Mvw^m \qquad (2)$$

or $$\log(v/u)=\log M+m\log w \qquad (3)$$

where u and w are functions expressed in terms of the titers of halogen, and k, M and m are constansts. With benzene as reactant, m was proved to be equal to 3.

This paper presents the results obtained from several series of experiments in which the rates of bromination of toluene in carbon tetrachloride were measured in the dark at 25°.

1. Determination of the Reaction Order (m) of Iodine Bromide.

Inserting the values obtained from the measurements into equation (3), a straight line relationship between $\log(v/u)$ and $\log w$ was ascertained, its slope being equal to 3 in this case too. Further calculation shows